

# Novel Adsorbent-Reactants for Treatment of Ash and Scrubber Pond Effluents

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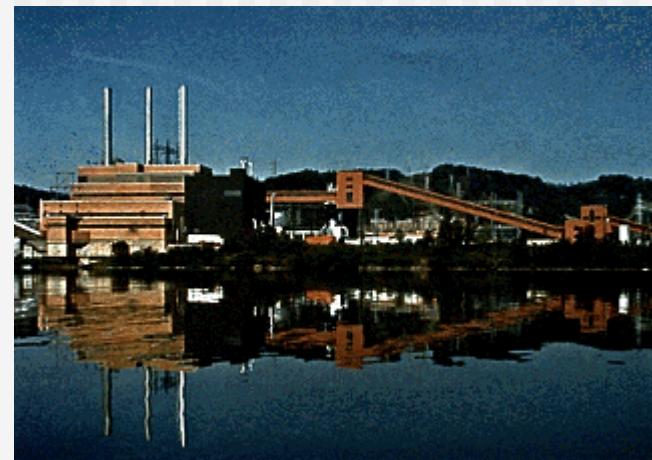
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# Overview

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- ❖ Background
- ❖ Project Objectives
- ❖ Methods
- ❖ Results
- ❖ Summary



# Background

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- Volatile Species
  - Arsenic
  - Mercury
  - Selenium
- Transfer to Water
  - FGD wastewater
  - Ash Pond water



# Background (As)

## ❖ Arsenic

- Arsenate, As(V), phosphate analog
  - $pK_1=2.2$ ,  $pK_2=7.0$ ,  $pK_3=11.5$
  - $\text{CaAsO}_4(\text{s})$ ,  $\text{BaAsO}_4(\text{s})$ ,  $\text{FeAsO}_4(\text{s})$
- Arsenite, As(III)
  - $pK_1=9.2$ ,  $pK_2=12.1$ ,  $pK_3=13.4$
  - $\text{As}_2\text{S}_3(\text{s})$
- Elemental, As(0)
  - Arsenopyrite ( $\text{FeAsS}$ ,  $\text{FeAs}_x\text{S}_{2-x}$ )
  - $\text{As}(0)(\text{s})$
- Arsenide, As(-III)

Periodic Table of Elements						
13 IIIA		14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
B	C	N	O	F	Ne	He
5 10.81 Boron	6 12.01 Carbon	7 14.01 Nitrogen	8 16.00 Oxygen	9 19.00 Fluorine	10 20.18 Neon	2 4.00 Helium
Al	Si	P	S	Cl	Ar	
13 26.98 Aluminum	14 28.0 Silicon	15 30.97 Phosphorus	16 32.07 Sulfur	17 35.45 Chlorine	18 39.95 Argon	
Ga	Ge	As	Se	Br	Kr	
31 69.72 Gallium	32 72.61 Germanium	33 74.92 Arsenic	34 78.96 Selenium	35 79.90 Bromine	36 83.80 Krypton	
In	Sn	Sb	Te	I	Xe	
49 114.82 Indium	50 118.71 Tin	51 121.76 Antimony	52 127.60 Tellurium	53 126.90 Iodine	54 131.29 Xenon	



# Background (Hg)

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## ❖ Mercury

### ■ Redox State

- Mercuric, Hg(II)
  - $\text{HgO(s)}$ ,  $\text{HgS(s)}$
  - $\text{HgCl}_2(\text{aq})$ ,  $\text{HgOHCl(aq)}$ ,  $\text{Hg(OH)}_2(\text{aq})$ ,  $\text{HgS(aq)}$
- Mercurous, Hg(I)
- Elemental, Hg(0)



# Background (Se)

## ❖ Selenium

- Selenate, Se(VI), sulfate analog
  - $pK_1 < 0$ ,  $pK_2 = 2.0$
  - $\text{BaSeO}_4(s)$
- Selenite, Se(IV), sulfite analog
  - $pK_1 = 2.6$ ,  $pK_2 = 8.3$
  - $\text{SeO}_2 + \text{H}_2\text{O} = \text{H}_2\text{SeO}_3$
- Elemental, Se(0)
- Selenide, Se(-II)

Periodic Table of Elements					
13 IIIA		14 IVA		15 VA	
B	C	N	O	F	Ne
5 10.81 Boron	6 12.01 Carbon	7 14.01 Nitrogen	8 16.00 Oxygen	9 19.00 Fluorine	10 20.18 Neon
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# Background

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- ❖ Summary – As, Hg, Se
  - Redox active; state important
  - Sulfide/Disulfide Solid phases
    - $\text{FeAsS}_{(\text{s})}$ ,  $\text{As}_2\text{S}_3_{(\text{s})}$
    - $\text{HgS}_{(\text{s})}$
    - $\text{FeSe}_{(\text{s})}$ ,  $\text{FeSeS}_{(\text{s})}$



# Background

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## ❖ Approach

- Remove target (As, Hg, Se)

- Pyrite ( $\text{FeS}_2(s)$ )
  - Iron Sulfide ( $\text{FeS}(s)$ )

- Surface Reaction

- Redox
    - Reduction; S(-II), Fe(II)
    - Oxidation; S(-I)
  - Precipitation ( $\text{FeAsS}(s)$ ,  $\text{As}_2\text{S}_3(s)$ ,  $\text{HgS}(s)$ ,  $\text{FeSe}(s)$ )



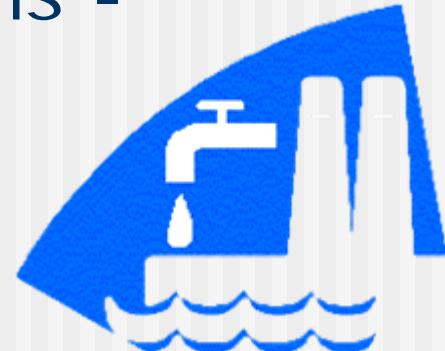
Solution → Surface → Products



# Project Objectives

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- ❖ Evaluate Adsorbent-Reactants for Removal and Stability
  - Develop Synthesis Techniques
  - Characterize Removal (pH,  $\text{SO}_4$ )
    - 5 Targets - As(III), As(V), Hg(II), Se(IV), Se(VI)
    - 2 Solids -  $\text{FeS}_2$ , FeS
  - Characterize Surface Reactions - Stability



# Methods

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- ❖ Experimental Plan (Removal)

- Batch System

- Kinetic
    - Removal Characteristics
      - Vary target concentration
      - Constant sorbent-reactant dose

- Effects

- pH (7, 8, 9, 10)
    - Sulfate (0, 1, 10 mM)



# Methods

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## ❖ Analytical Methods

### ■ Arsenic

- HGAAS (form  $\text{AsH}_3$  with  $\text{NaBH}_4$ )
- Speciation by pH (form  $\text{AsH}_3$  with  $\text{NaBH}_4$ )
  - Total - Low pH reduction
  - As(III) - Moderate pH reduction
  - As(V) – Difference

### ■ Mercury

- Cold Vapor AAS (reduction with  $\text{NaBH}_4$ )

### ■ Selenium

- HGAAS ( $\text{Se(IV)} + \text{NaBH}_4$ )
- $\text{Se(VI)} + \text{HCl} = \text{Se(IV)}$

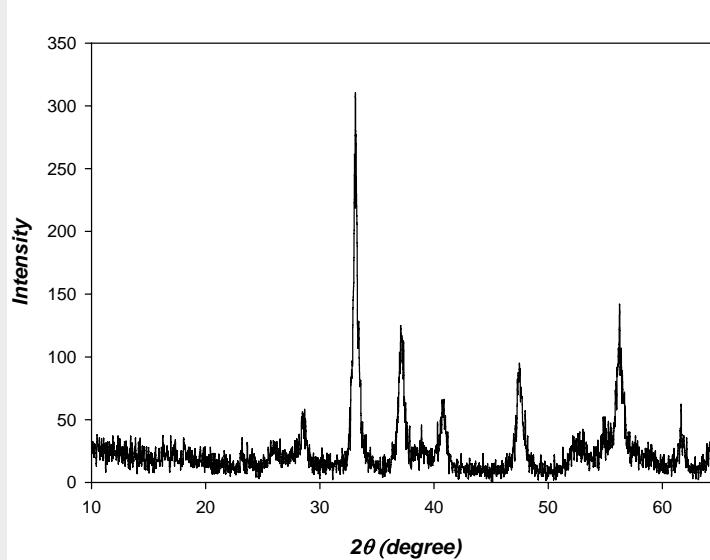


# Methods (Synthesis)

❖ Pyrite Synthesis (Wei, et al. 1997, modified)

- $2\text{HS}^- + 2 \text{Fe}^{3+} = \text{FeS}_2 + 2\text{H}^+ + \text{Fe}^{2+}$
- 60 °C

XRD



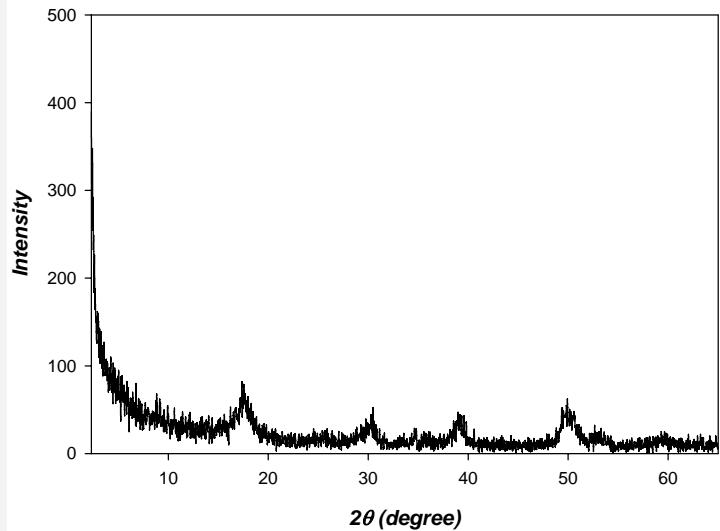
TEM



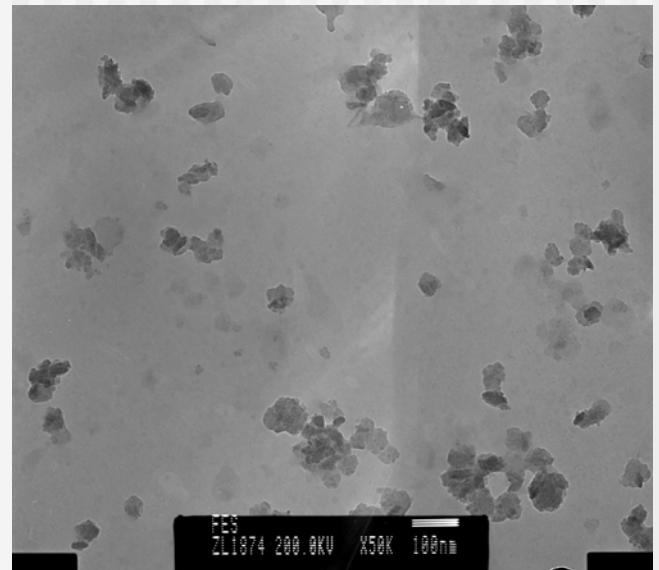
# Iron Sulfide Synthesis



XRD



TEM



# Results – As(III) Summary

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- ❖ pH

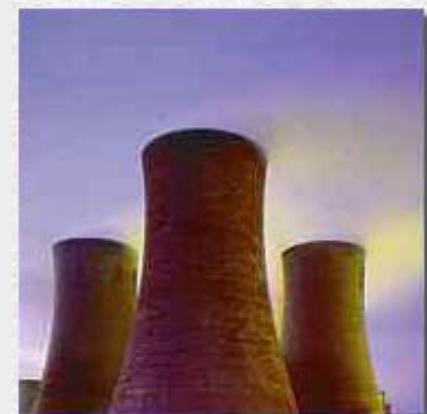
- Pyrite – higher pH increases loading
- FeS – optimum pH 8-9

- ❖  $\text{SO}_4$

- Small effect on pyrite
- Moderate effect on FeS

- ❖ Pyrite/FeS

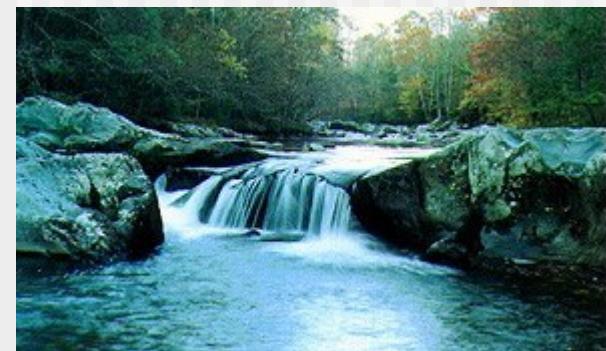
- Loadings similar
- More surface reaction on FeS



# Results – As(V) Summary

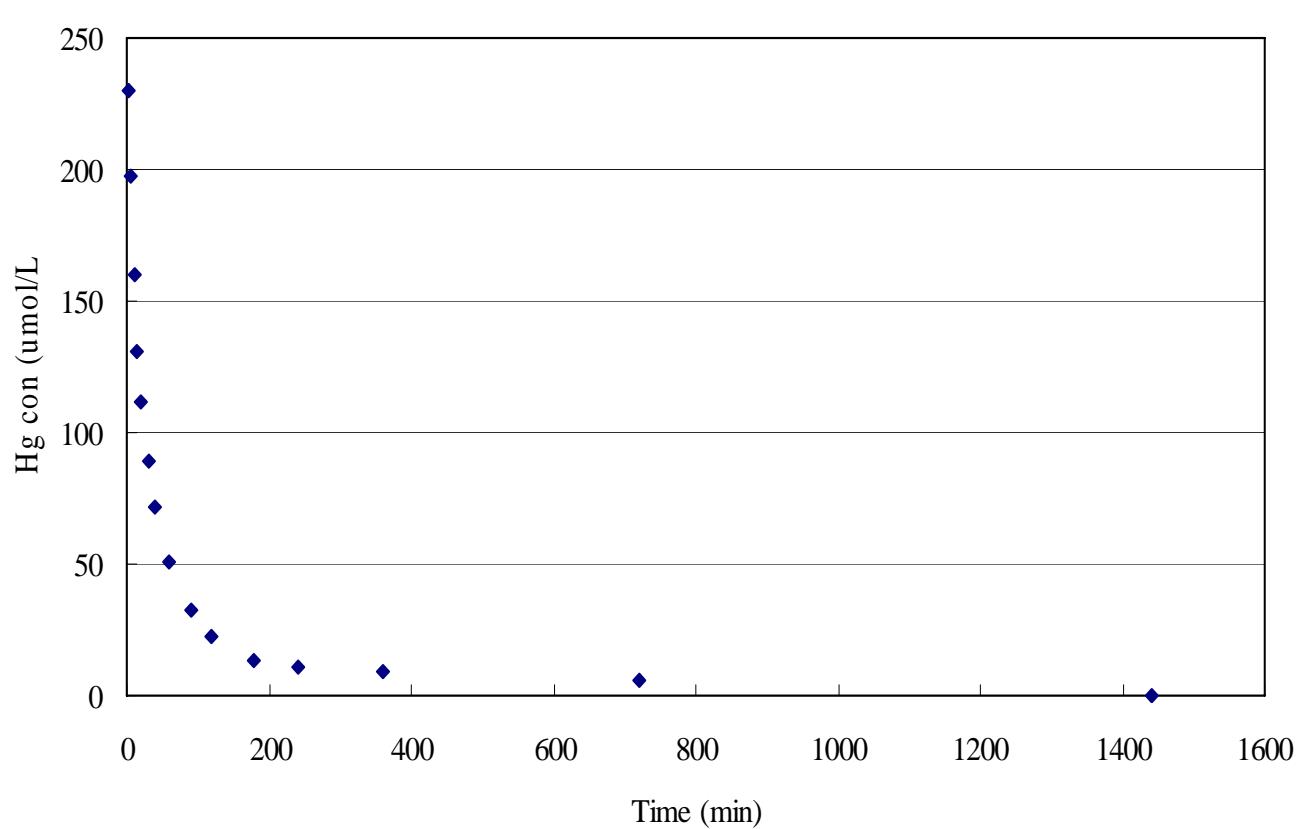
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- ❖ pH
  - Pyrite – optimum pH 8-9
  - FeS – strong effect, higher loading at lower pH
- ❖  $\text{SO}_4$ 
  - Pyrite – small effect
  - FeS – moderate effect
- ❖ Pyrite/FeS
  - pH response different
  - FeS higher loading at low pH
  - FeS more surface reaction



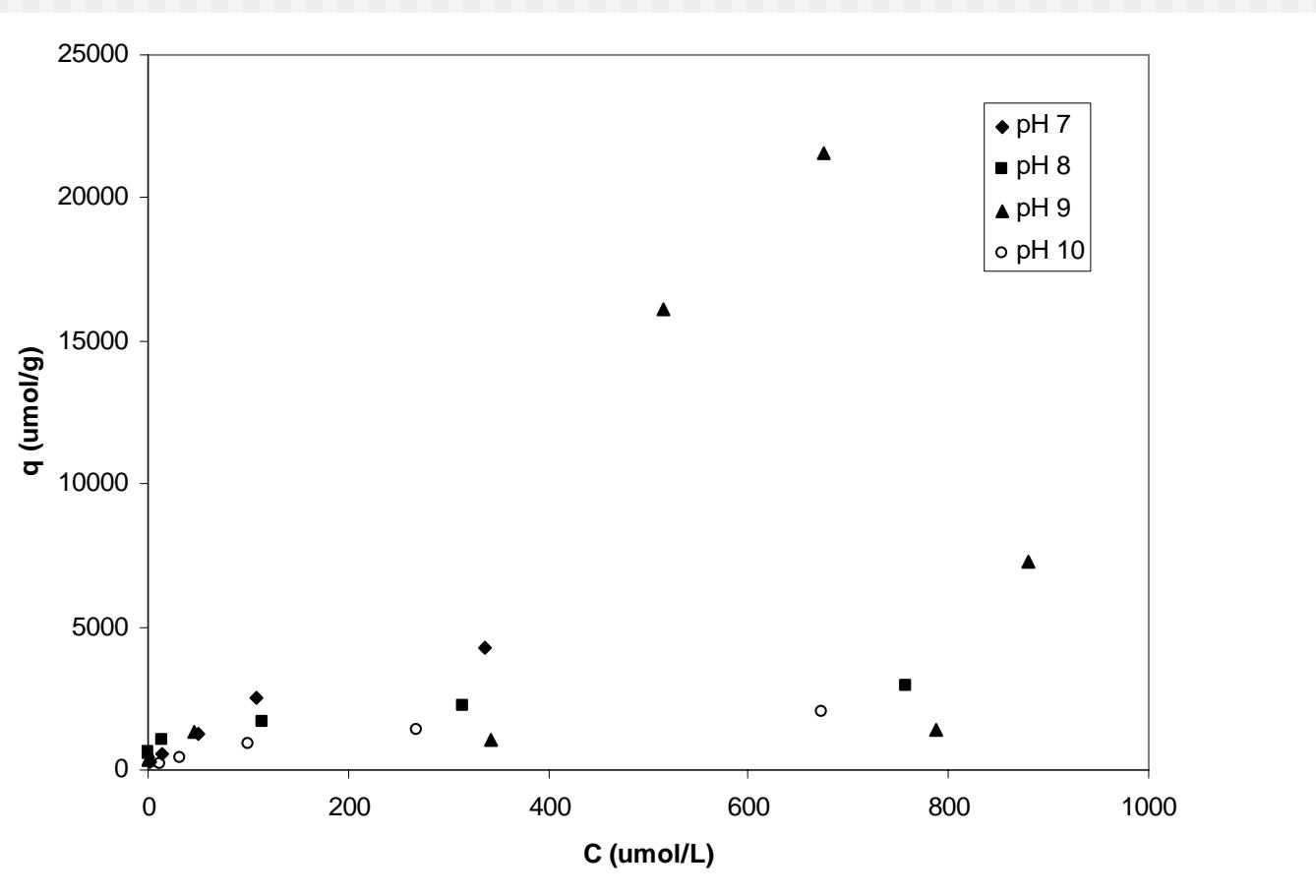
# Results - Hg

## ❖ Pyrite/Kinetics



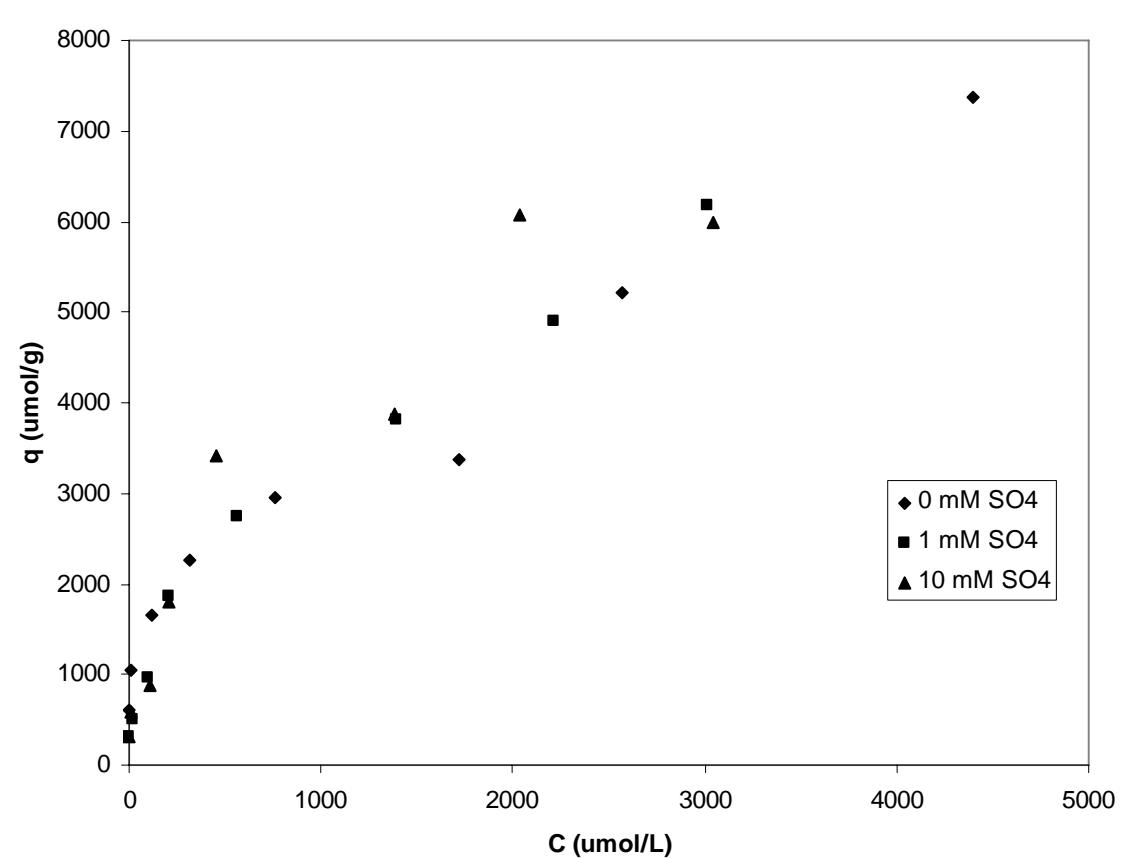
# Results - Hg

## ❖ Pyrite/pH



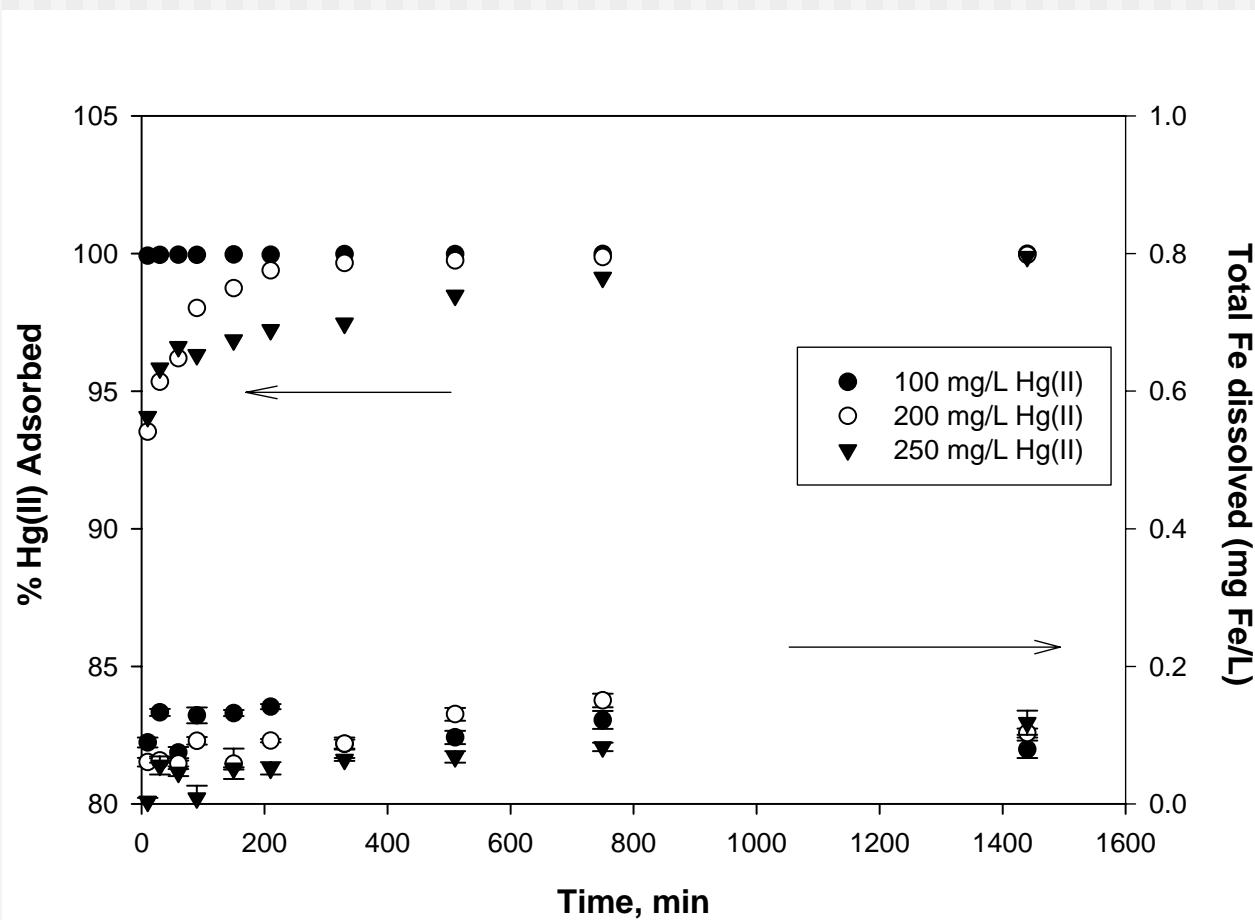
# Results – Hg

## ❖ Pyrite/SO<sub>4</sub>



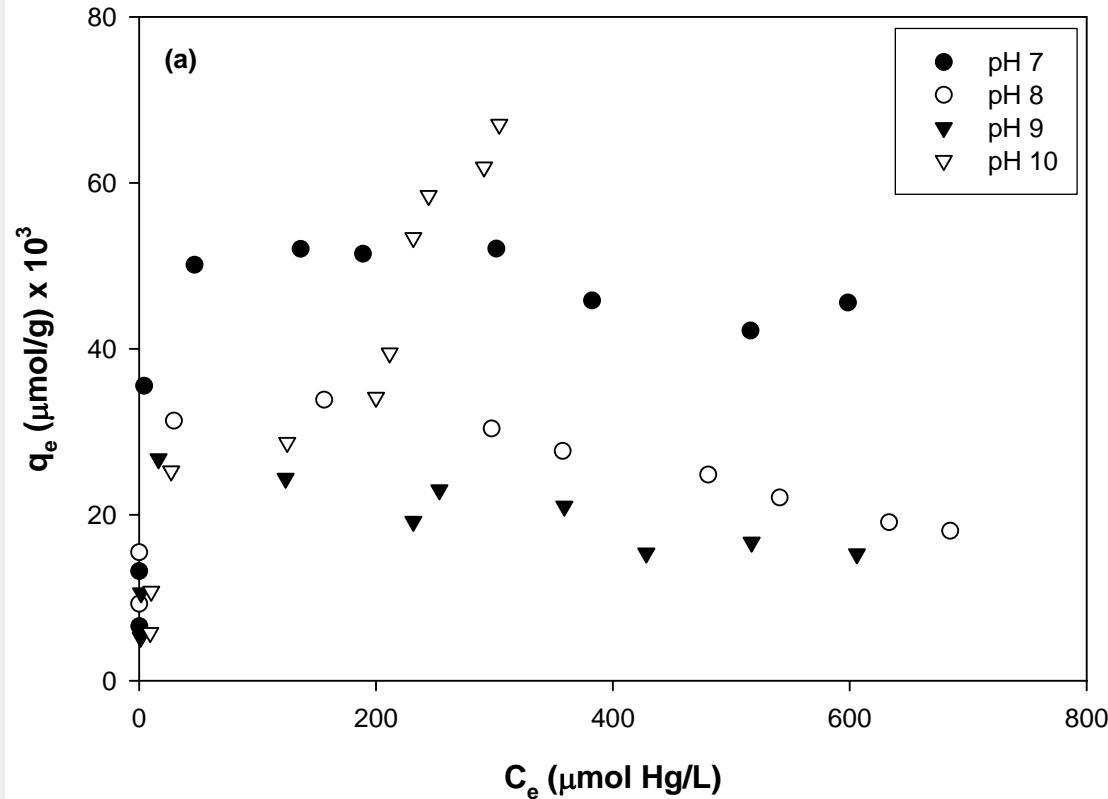
# Results - Hg

## ❖ FeS/Kinetics



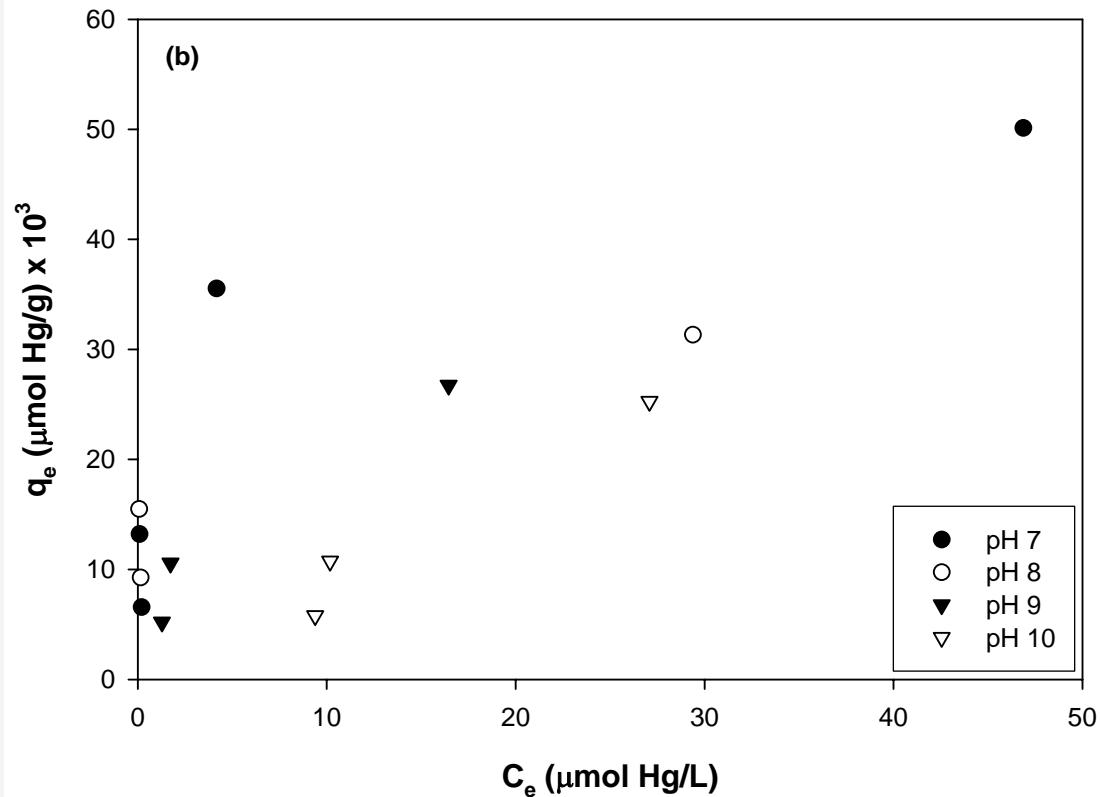
# Results - Hg

## ❖ FeS/pH



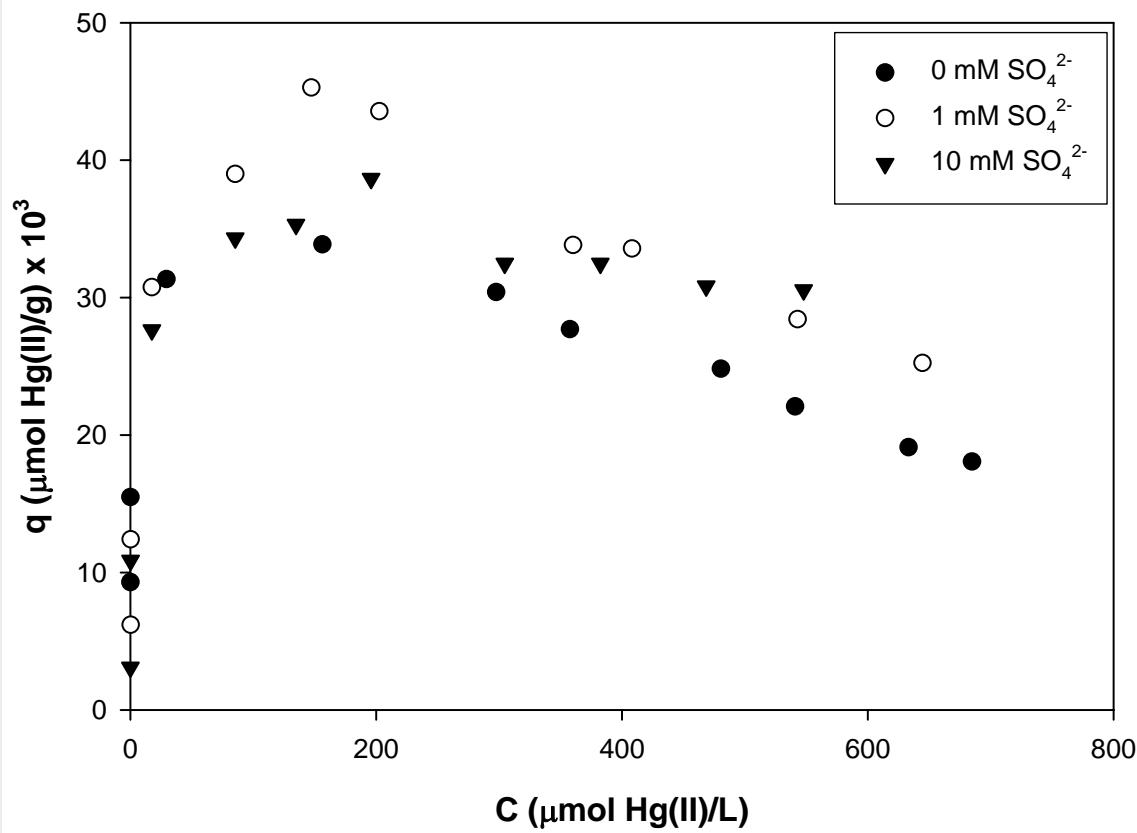
# Results - Hg

## ❖ FeS/pH (low conc.)



# Results - Hg

## ❖ FeS/SO<sub>4</sub>



# Results – Hg Summary

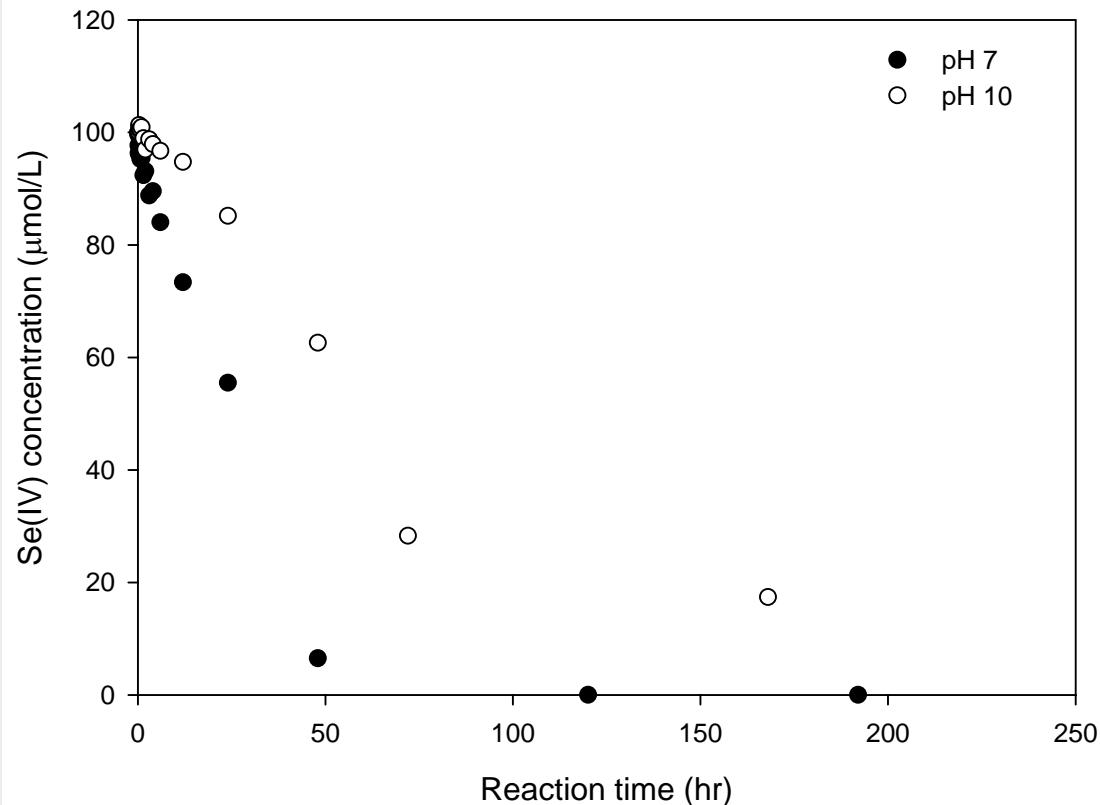
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- ❖ Very high loading, 10x As
- ❖ pH – no strong effect
- ❖ High variability – surface reactions
- ❖  $\text{SO}_4$ 
  - $\text{FeS}_2$  – little effect
  - $\text{FeS}$  – small positive effect



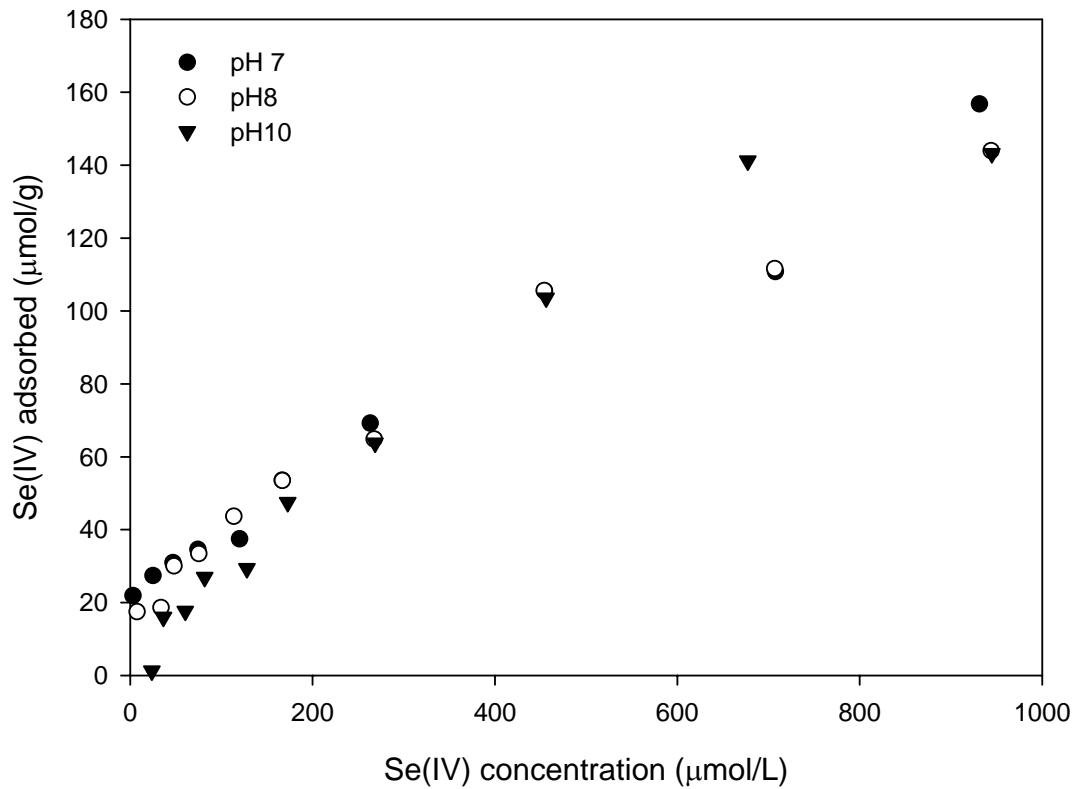
# Results – Se(IV)

## ❖ Pyrite/Kinetics



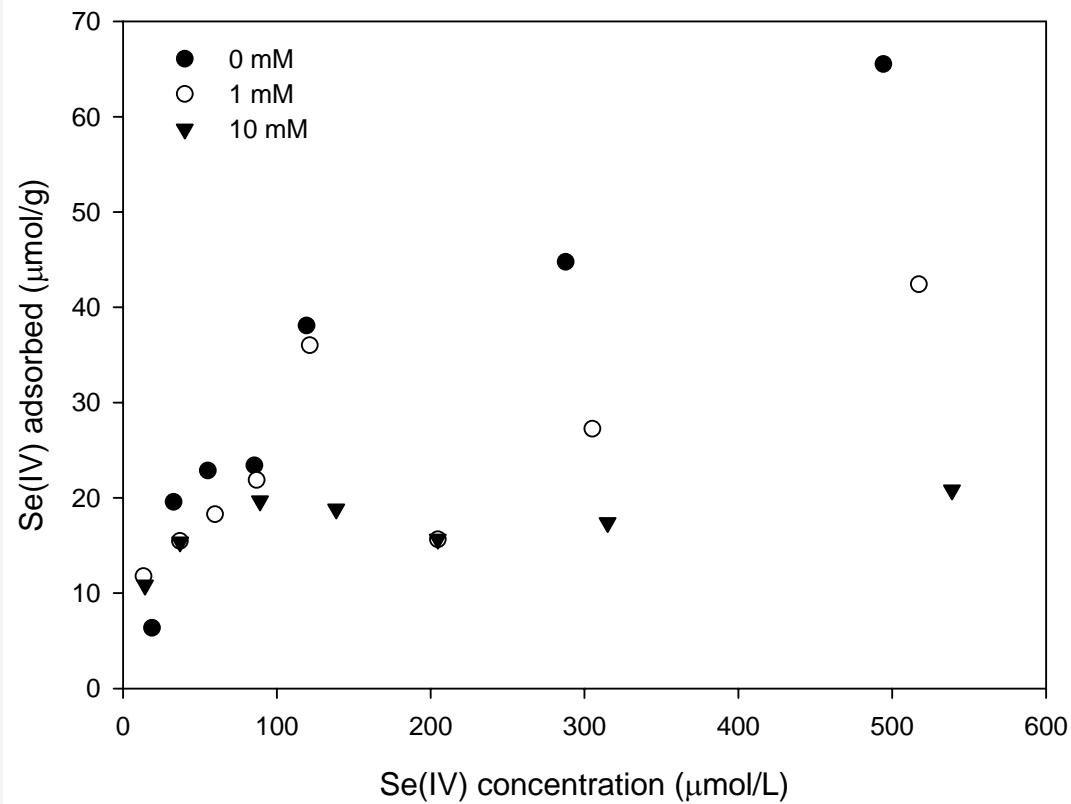
# Results – Se(IV)

## ❖ Pyrite/pH



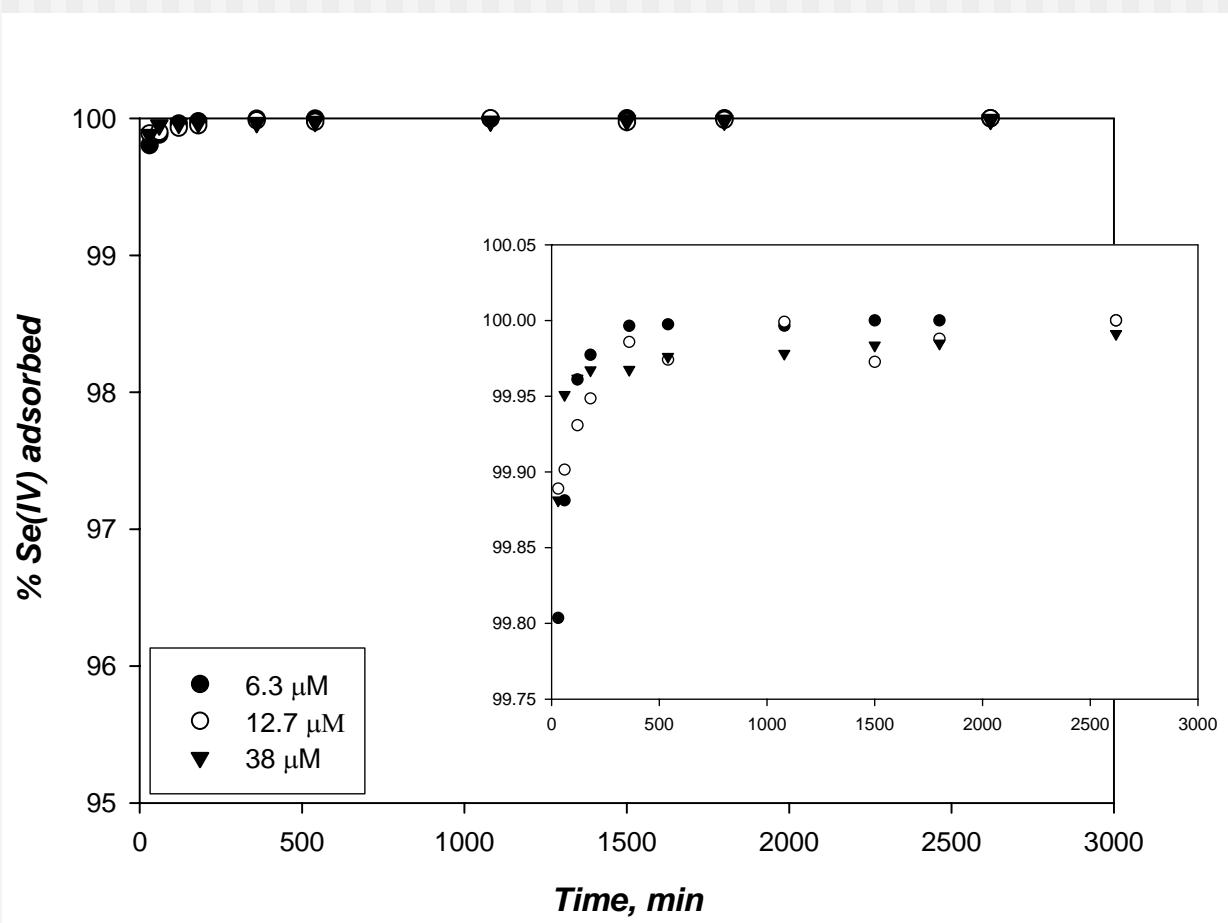
# Results – Se(IV)

## ❖ Pyrite/SO<sub>4</sub>



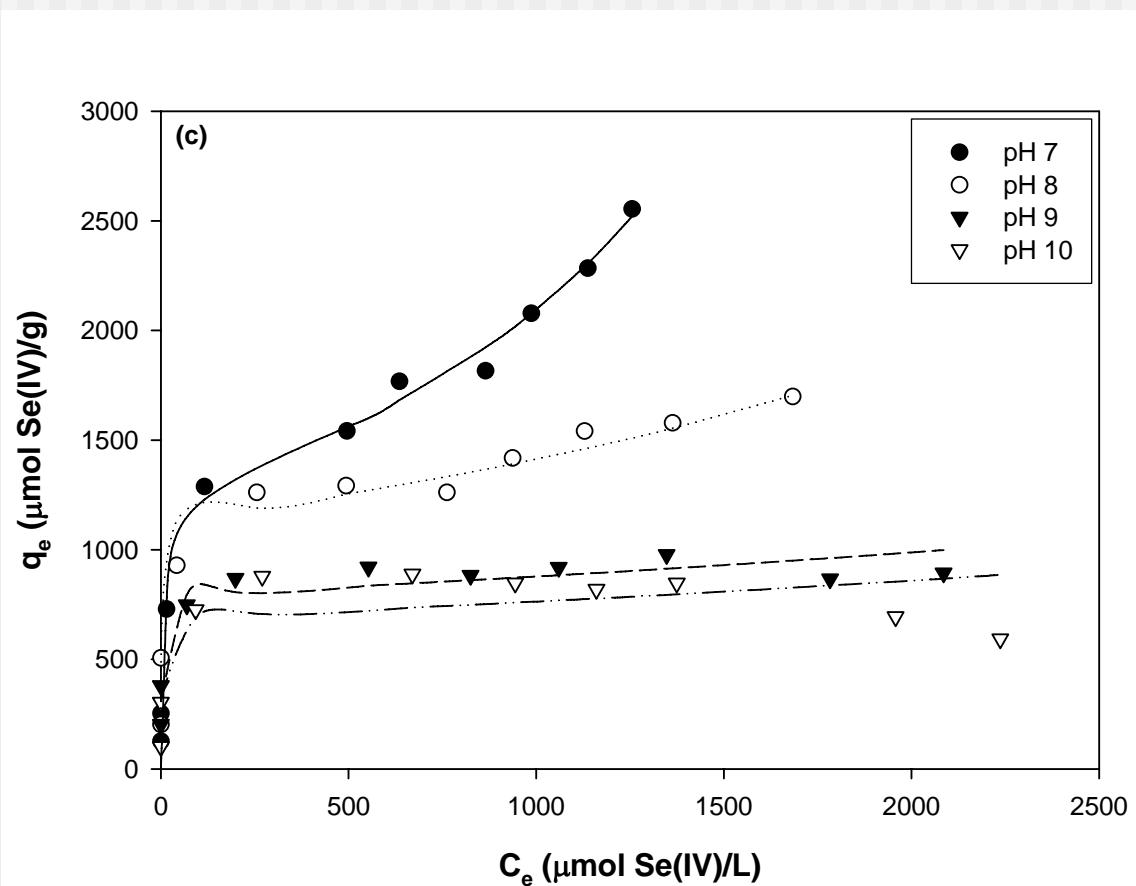
# Results – Se(IV)

## ❖ FeS/Kinetics



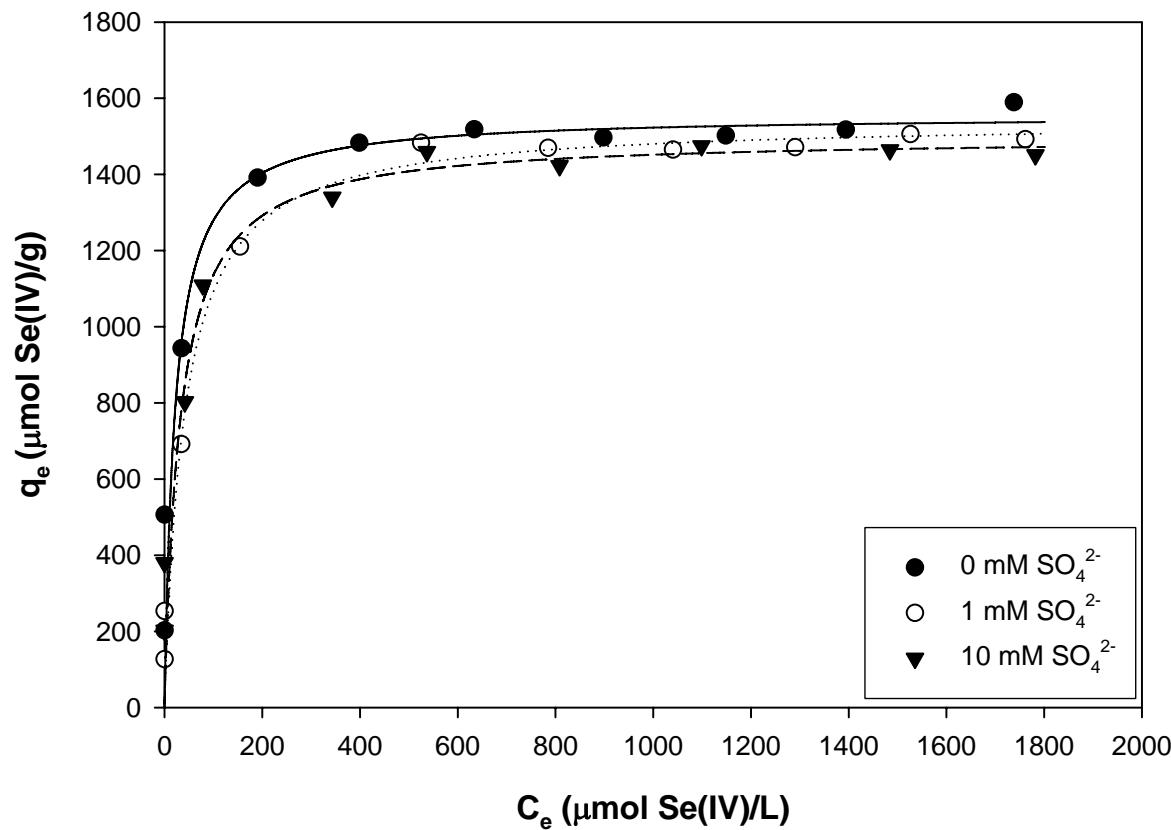
# Results – Se(IV)

## ❖ FeS/pH



# Results – Se(IV)

## ❖ FeS/SO<sub>4</sub>



# Results – Se(IV) Summary

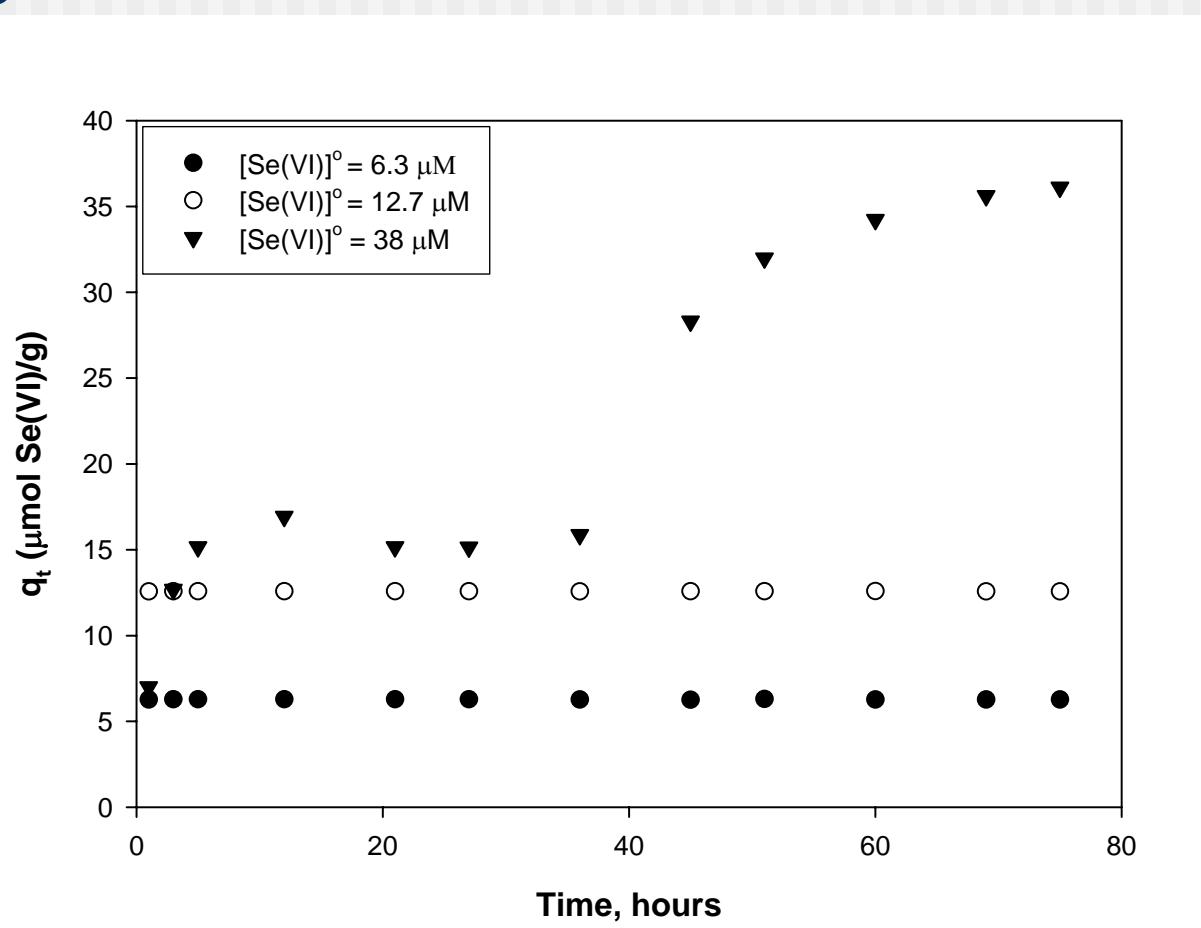
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- ❖ Kinetics
  - Pyrite - slow
  - FeS - fast
- ❖ pH
  - Pyrite - small
  - FeS - pH 7>pH8>pH9,10
- ❖ SO<sub>4</sub>
  - Pyrite - moderate at high loading
  - FeS - small



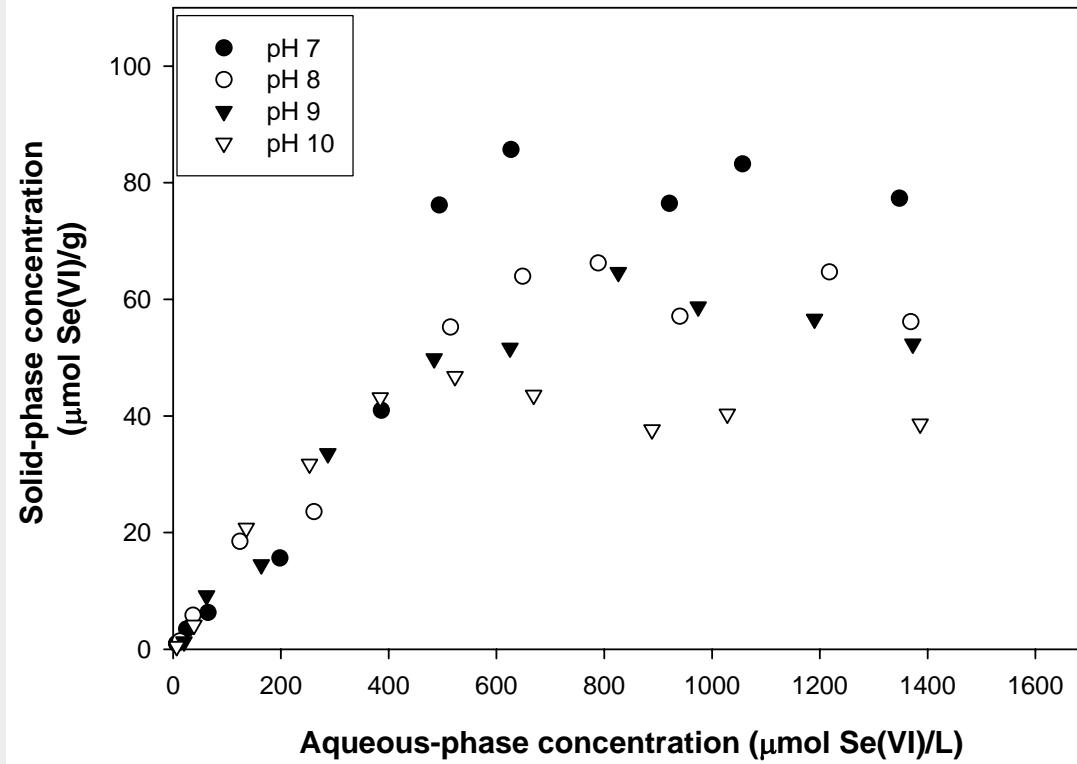
# Results – Se(VI)

## ❖ Pyrite/Kinetics



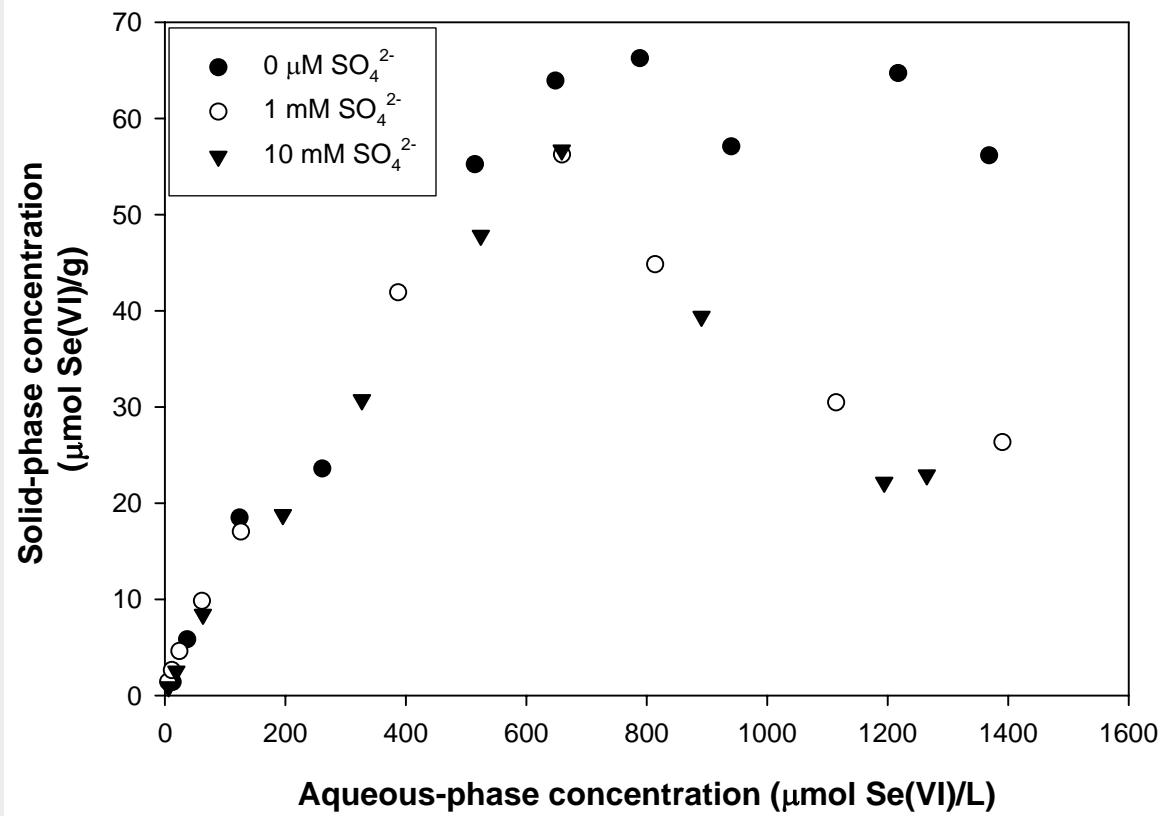
# Results – Se(VI)

## ❖ Pyrite/pH



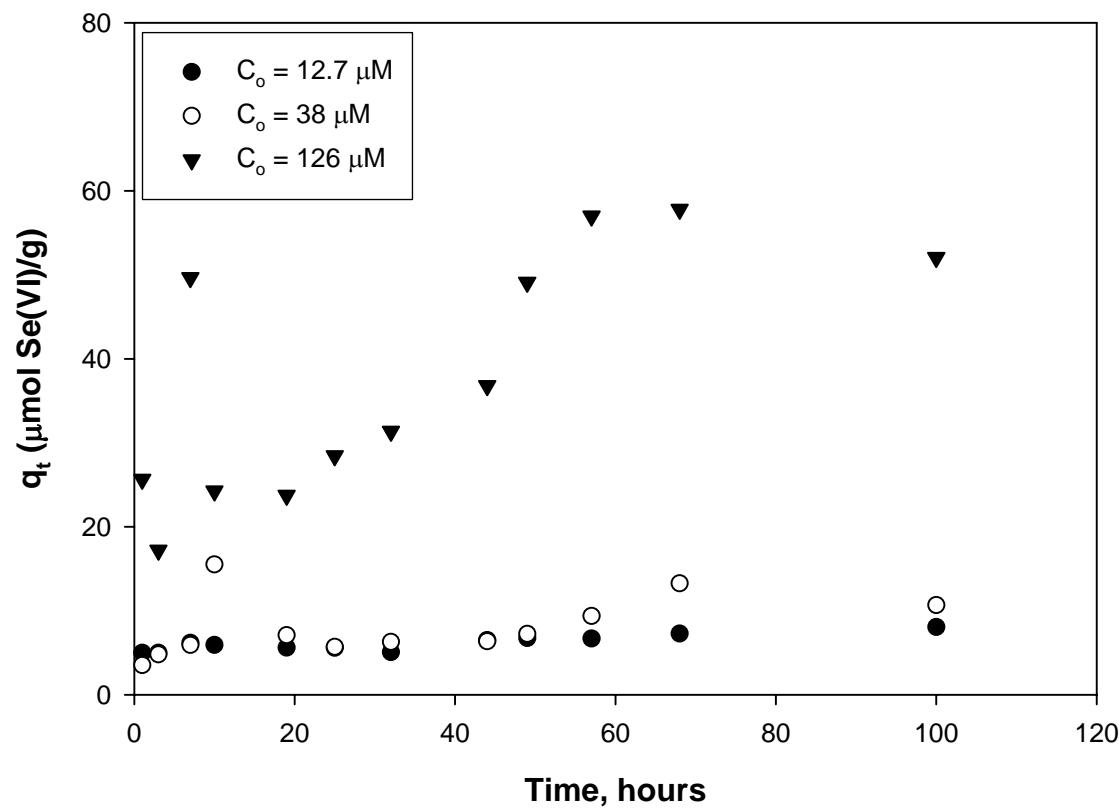
# Results – Se(VI)

## ❖ Pyrite/SO<sub>4</sub>



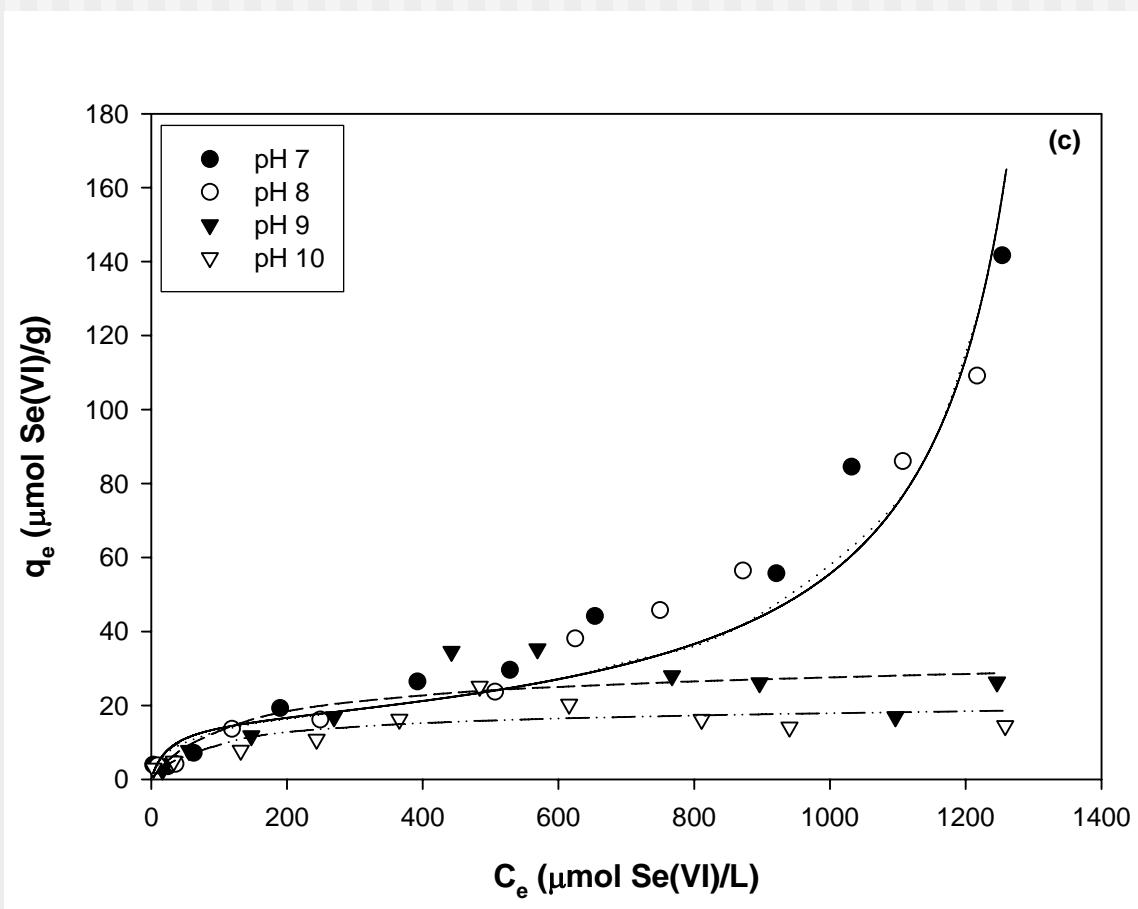
# Results – Se(VI)

## ❖ FeS Kinetics



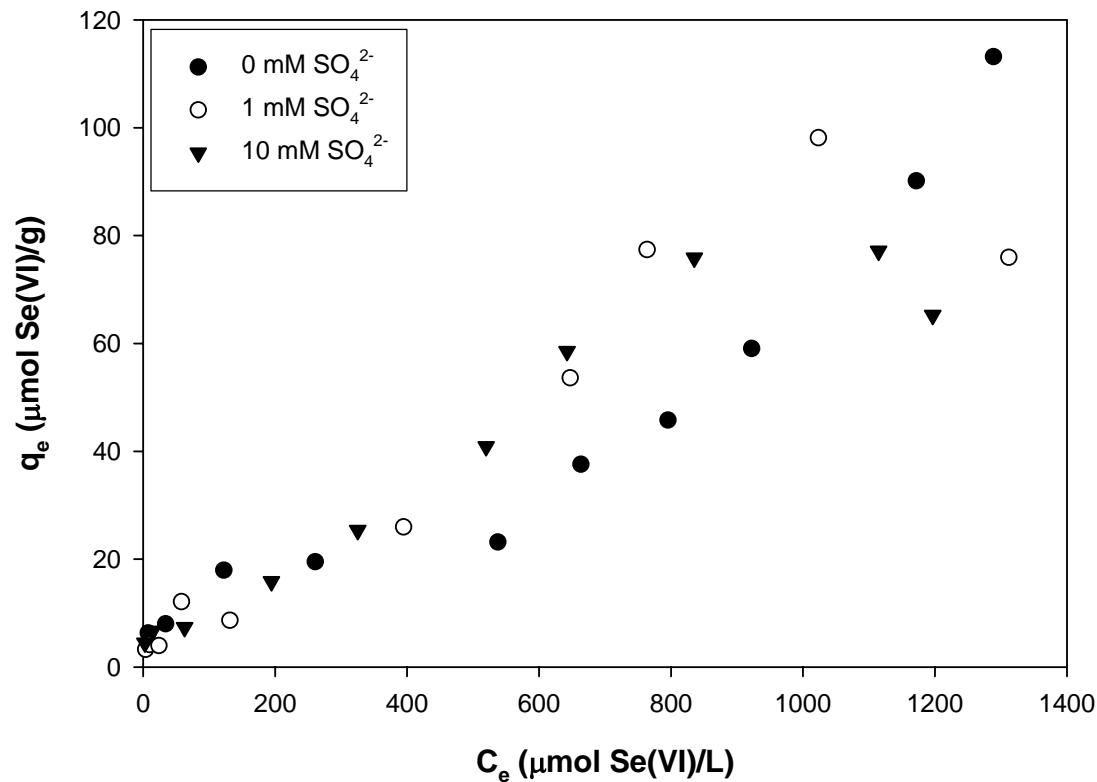
# Results – Se(VI)

## ❖ FeS/pH



# Results – Se(VI)

## ❖ FeS/SO<sub>4</sub>



# Results – Se(VI) Summary

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- ❖ Kinetics (Pyrite, FeS)
  - Fast plateau, continue high loading
- ❖ pH
  - Pyrite – none at low, moderate at high loading
  - FeS – small at low loading; BET pH 7,8
- ❖ SO<sub>4</sub>
  - Pyrite – none at low loading; inverse BET
  - FeS – small, mixed



# Summary

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- ❖ Adsorbent-Reactants Effective
  - Removal
    - $\text{FeS} > \text{FeS}_2$
    - Hg much greater
    - Sulfate low to moderate effect
  - Stability (?)
- ❖ Sorption and Reaction
  - Slow removal
  - BET



# Questions

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